

Supplementary Information

Tunable Anisotropic Heat Transport in Structurally and Chemically Modified 3D Graphene

S1. Chemical Modification of Three-Dimensional Graphene

A. Polymer and Molecular n-Type Doping

Pristine three-dimensional graphene (3DG) samples were chemically modified using four n-type dopants: branched polyethyleneimine (PEI), thermally activated polyethyleneimine (PEI-A), 4-(2,3-dihydro-1,3-dimethyl-1H-benzimidazol-2-yl)-N,N-dimethylbenzenamine (N-DMBI), and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD). Poly(vinylpyrrolidone) (PVP) was also investigated as a weak polymeric n-type dopant for comparison. Procedures were adapted from our previous thermoelectric studies of 3DG.[1]

For PEI doping, branched polyethyleneimine ($M_w \approx 25,000$, Sigma-Aldrich) was dissolved in ethanol to prepare solutions corresponding to final dopant loadings of 0.25, 0.50, 0.75, and 1.00 wt.%. The solutions were drop-cast onto pristine 3DG and allowed to dry under ambient conditions. PEI-A samples were prepared by first doping the samples with PEI as described above. The PEI-treated samples were subsequently annealed at 180 °C for 1 h under flowing nitrogen atmosphere (5 SLM) to deprotonate amine groups and enhance electron donation to the graphene network.[1]

For N-DMBI doping, 4-(2,3-dihydro-1,3-dimethyl-1H-benzimidazol-2-yl)-N,N-dimethylbenzylamine was dissolved in chlorobenzene and drop-cast onto pristine 3DG to obtain final loadings of 0.25, 0.50, 0.75, and 1.00 wt.%. Following solvent evaporation, samples were annealed at 80 °C for 20 min under nitrogen to activate the dopant.[1,2]

For TBD doping, 1,5,7-triazabicyclo [4.4.0] dec-5-ene was dissolved in acetone and applied to pristine 3DG using the same concentration series. Doping was performed inside an inert atmosphere glovebox (95% Ar/5% H₂) to minimize exposure to oxygen and moisture during processing.[1,3]

For PVP doping, poly(vinylpyrrolidone) was dissolved in ethanol and deposited onto pristine 3DG at concentrations corresponding to 0.25, 0.50, 0.75, and 1.00 wt% loading. Samples were allowed to dry under ambient conditions after solvent evaporation.[1]

B. Acid treatments

P-type modification was performed using sulfuric acid (95-98%, ACS reagent grade) and nitric acid (68-70%, ACS reagent grade). Pristine 3DG samples were immersed in the acid bath for 1, 2.5, 5, or 10 min at room temperature.[1]

Following treatment, samples were immediately rinsed in deionized water for 1 min and subsequently rinsed in ethanol for 30s to remove residual acid and minimize continued

oxidation. The treated samples were dried on a hot plate at 90 °C for 10 min prior to characterization and thermal-conductivity measurements.

C. Selection of Chemical Treatments

The selected dopants span a range of doping mechanisms, including polymer-mediated electron donation (PEI, PEI-A, PVP), molecular charge-transfer doping (N-DMBI and TBD), and oxidative p-type surface treatments (sulfuric acid and nitric acid). This treatment matrix was adopted from previous studies on 3DG thermoelectric materials because it produced measurable changes in carrier concentration, Seebeck coefficient, and electrical conductivity while maintaining the structural integrity of the freestanding graphene network.[1]

For the present study, these identical processing conditions were used to investigate how chemical modification influences directional heat transport in 3DG without introducing substantial changes to the macroscopic network architecture.

S2. Cross-Plane Thermal Conductivity by Differential 3 ω Method

A. Measurement principle, heater platform and resistance thermometry

Cross-plane thermal conductivity, $\kappa_{\perp}$, was determined using a differential 3 ω method based on the established electrothermal line-heater technique of Cahill and its subsequent extensions to thin films and multilayer structures.[4–7] In the conventional 3 ω configuration, a narrow metal line serves simultaneously as a periodic heat source and resistance thermometer. The frequency-domain measurement is advantageous for the present porous architecture because the thermal probing depth can be varied without requiring direct optical access to the graphene network. For an applied current $I(t) = I_0 \sin(\omega t)$, Joule heating contains a component at twice the electrical excitation frequency, $P_{2\omega} = I_0^2 R_0 / 2$, which produces a periodic heater-temperature response at 2ω . Over the relatively small temperature oscillations used here, the heater resistance is represented locally as $R(T) = R_0 [1 + \beta(T - T_0)]$, where R_0 is the resistance at the reference temperature and $\beta = (1/R_0)(dR/dT)$ is the heater temperature coefficient (TCR). Mixing of the resistance oscillation at 2ω with the electrical current ω generates a voltage component at 3ω . Using a consistent peak-amplitude convention, $V_{3\omega} = (1/2)(I_0 R_0 \beta \Delta \overline{T_{2\omega}})$, and $\Delta \overline{T_{2\omega}} = (2V_{3\omega}) / (V_{1\omega} \beta)$. Here, $\Delta \overline{T_{2\omega}}$ denotes the complex temperature oscillation. Both in-phase and quadrature components of the harmonic response were recorded to verify the expected frequency-domain behavior, while the in-phase temperature response was used for the differential conductivity analysis.

The heater resistance was calibrated as a function of temperature before thermal measurements using sufficiently small electrical excitation to avoid appreciable self-heating. Representative metal lines exhibited an approximately linear $R(T)$ response over the temperature interval relevant to the room-temperature measurements and remained stable over repeated thermal cycling. The experimentally determined dR/dT was used for converting the harmonic voltage response to temperature.

Because 3DG is porous, electrically conductive, and mechanically compliant, direct metal patterning on the graphene surface could introduce electrical leakage, processing damage, and poorly defined heater geometry. The heater/thermometer was therefore fabricated by standard thin-film microfabrication on an electrically insulating polyimide support and subsequently transferred to the measurement stack. The nominal polyimide thickness used for the 3DG measurements was approximately 25 μm . The heater width and active length were characterized independently, and their measured values were used in the thermal reduction. This transferable configuration provides a reproducible heater geometry while avoiding direct lithographic processing of the 3DG. Finite heater dimensions were considered through the standard finite-width line-heater formulation. The working frequency range was selected such that the thermal penetration depth was large relative to the heater half-width while remaining small relative to the heater active length and substrate dimensions ($b \ll \lambda \ll \ell$), thereby limiting finite-width and end effects.

B. Differential thermal resistance, data reduction, calibration and validation

For multilayer 3ω measurements, the measured harmonic response contains contributions from the heater, polyimide support, interfaces, sample, and substrate. Differential subtraction removes the components common to the control and sample configurations, after which the independently calibrated interface contribution is applied to obtain the corrected sample response.[5,6] Two nominally matched configurations were measured, heater/PI/substrate as the control and heater/PI/3DG/substrate as the sample stack. The differential temperature response was defined as $\Delta T_{diff} = \text{Re}[\widetilde{\Delta T_{stack}} - \widetilde{\Delta T_{control}}]$. Subtracting the control suppresses thermal contributions common to the heater, polyimide support, and substrate, leaving the added thermal impedance associated with insertion of the 3DG layer and any residual interface terms introduced by that insertion. Frequency selection was guided by the thermal penetration depth and the frequency range over which the differential response remained stable.

For a thermal oscillation at frequency $f_{2\omega}$, $\delta = \sqrt{\frac{D}{\pi f_{2\omega}}}$, where D is the relevant thermal diffusivity. The analysis was restricted to the region in which the thermal field sampled the inserted layer and support stack and the differential response was approximately

stable with frequency. For an active heater of half-width b and line heating power P' in W m^{-1} , the nominal heat flux beneath the heater is written as $q'' = P'/2b$. The corresponding area-normalized differential resistance is $R''_{\perp} = \Delta T_{diff}/q''$. Assigning this differential resistance to a 3DG layer of measured thickness t gives the reported cross-plane thermal conductivity, $\kappa_{\perp} = t/R''_{\perp}$. The $R''_{\perp}$ was used when comparing rolled and welded structures because thermal resistances, unlike apparent conductivities, combine directly in series. The same heater geometry, substrate, assembly protocol, and contact procedure were maintained across the sample series, and residual stack-to-stack variation was included in the measurement uncertainty.

The measurement platform was validated sequentially before application to 3DG. The objective was to test different elements of the data-reduction chain: bulk frequency-domain transport, thin-film differential subtraction, the polyimide-supported heater architecture, and a conductive anisotropic reference material. For a semi-infinite homogeneous substrate, the in-phase temperature oscillation varies approximately linearly with $\ln(2\omega)$, $\text{Re}(\Delta T_{2\omega}) = C - [(P'/2\pi\kappa)\ln(2\omega)]$, such that the slope provides an independent determination of the substrate thermal conductivity.[8] This was applied to crystalline silicon consistent with accepted room-temperature values. A thermally grown SiO_2 layer on Si was then used to test the differential thin-film treatment. The Si and SiO_2 measurements yielded values consistent with accepted room-temperature references, validating both the conventional slope analysis and differential thin-film reduction. Agreement among the Si, SiO_2 and graphite validation measurements is summarized in Figure S3(a).

The transferable polyimide support required a separate calibration because its resistance and its physical contact with the underlying stack are present in every 3DG measurement. Two polyimide thicknesses, approximately 12.7 and 25.4 μm , were evaluated under matched conditions. The corresponding two-thickness measurement configurations are illustrated in Figure S3(e,f). After subtraction of the common substrate response, the effective area-normalized resistance of the polyimide-supported configuration was expressed as $R''_{PI,eff} = \langle \Delta T_{PI} \rangle / q''$. Because the two measurements differed only in polyimide thickness, the common background contribution cancels when their resistances are differenced, giving $\kappa_{PI} = \Delta d_{PI} / \Delta R''_{PI} \approx 0.22 \pm 0.02 \text{ W m}^{-1} \text{ K}^{-1}$ with the corresponding effective resistances shown in Figure S3(g). The two polyimide thicknesses allow the thickness-dependent film contribution to be distinguished from the approximately thickness-independent interface contribution under matched assembly conditions. The measured frequency-dependent responses are shown in Figure S3(h), and the corresponding effective area-normalized resistances are summarized in Figure S3(g). Finally, the complete transferable-heater/differential-stack configuration was tested using a graphite sheet, providing a conductive and strongly anisotropic benchmark closer to the thermal regime relevant to 3DG. The extracted cross-plane

conductivity was $\kappa_{\perp, \text{graphite}} = 6.4 \pm 0.8 \text{ W m}^{-1} \text{ K}^{-1}$, consistent with the established room-temperature cross-plane conductivity range of graphite[9]; the corresponding differential response is shown in Figure S3(c). The agreement with the established cross-plane conductivity of graphite provides an experimental validation of the complete heater geometry, interface treatment, frequency selection, and differential data-reduction procedure used subsequently for 3DG.

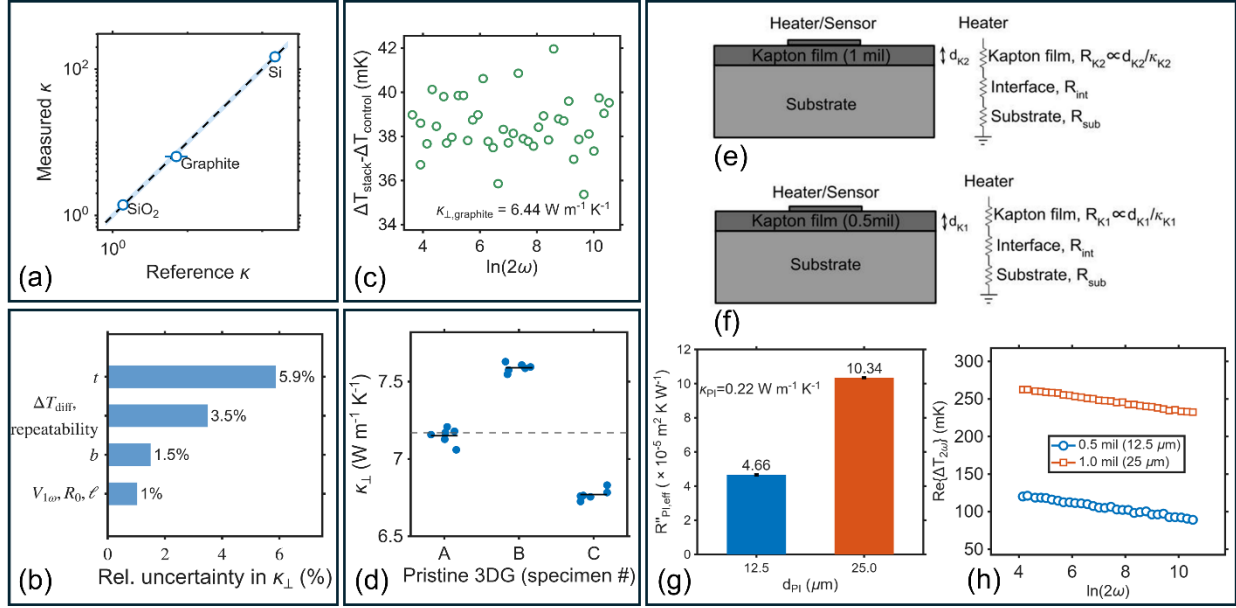


Figure S3. Validation and uncertainty of the differential 3ω cross-plane measurement. (a) Measured versus reference thermal conductivity for Si, SiO_2 , and graphite. (b) Relative measurement-uncertainty components. (c) Differential graphite response. (d) Repeat measurements of pristine 3DG, (e, f) Two-thickness polyimide calibration configurations. (g) Effective polyimide thermal resistance. (h) Polyimide temperature response versus frequency.

C. Uncertainty and reproducibility

The cross-plane conductivity follows from $\kappa_{\perp} = (P't)/(2b\Delta T_{diff})$, so its uncertainty is governed principally by the electrical heating power, sample thickness, heater geometry, temperature calibration, differential temperature response, uncertainty in the calibrated interface correction, and assembly repeatability. For statistically independent quantities x_i , the combined standard uncertainty was evaluated using first-order propagation,

$$u_c^2(\kappa_{\perp}) = \sum_i \left(\frac{\partial \kappa_{\perp}}{\partial x_i} u(x_i) \right)^2. \text{ For the directly multiplicative terms, } \left[\frac{u_c(\kappa_{\perp})}{\kappa_{\perp}} \right]^2 \approx \left[\frac{u(P')}{P'} \right]^2 +$$

$$\left[\frac{u(t)}{t} \right]^2 + \left[\frac{u(b)}{b} \right]^2 + \left[\frac{u(\Delta T_{diff})}{\Delta T_{diff}} \right]^2. \text{ The uncertainty associated with } \Delta T_{diff} \text{ represents the}$$

repeatability of the measured differential harmonic response, including finite averaging

and TCR calibration. The baseline instrument/geometry characterization gave representative standard uncertainties of approximately 0.5% in the fundamental heater voltage, 0.02% in four-probe heater resistance, 1.5% in heater half-width, 0.25% in active heater length, and approximately 3.5% in the low-frequency differential temperature mean. Sample thickness uncertainty was evaluated separately for each 3DG specimen because it becomes increasingly important for thin and mechanically compressed samples. The relative contributions of the principal measurement quantities are summarized in Figure S3(b).

Uncertainty associated with the polyimide-platform calibration was propagated together with the electrical, geometrical, and temperature-response terms. Additional assembly-to-assembly and specimen-to-specimen variability was evaluated experimentally using repeat measurements at multiple locations on independent pristine 3DG specimens (Figure S3(d)) and is represented by the observed measurement scatter.

S3. In-Plane Thermal Conductivity by Suspended Electrothermal Measurement

A. Resistance thermometry and effective thermal resistance

In-plane thermal conductivity, $\kappa_{\parallel}$, was determined using a suspended four-probe electrothermal method in which the electrically conductive 3DG strip served simultaneously as the Joule heater and resistance thermometer. Electrical heating combined with resistance thermometry is well established for thermal characterization of suspended conductive microstructures, where the temperature-dependent electrical resistance provides a measure of the specimen temperature rise.[10] Related self-heating/resistance-thermometry approaches have also been applied to graphene-derived films.[11] For each material condition, nominal suspended lengths l of 7, 10, and 15 mm were measured using strips approximately 2mm wide. The specimen cross-sectional area was $A = wt$, where w and t are the measured width and thickness.

A four-probe electrical configuration was used so that electrical lead and contact resistance did not contribute to the resistance measured across the active suspended section. Before self-heating measurements, the specimen resistance was calibrated as a function of temperature. Over the measurement interval, the local resistance response was represented as $R(T) = R_0 [1 + \beta(T - T_0)]$, where $\beta = (1/R_0)(dR/dT)$ is the temperature coefficient of resistance. During Joule heating, the measured resistance change was converted to the resistance-derived average temperature rise, $\overline{\Delta T} = \Delta R / \beta R_0$. The electrical power dissipated in the active section was obtained from $P = IV$, and measurements were restricted to the regime in which the resistance change was reversible and approximately proportional to heating power. The resulting effective

thermal resistance was obtained from, $\overline{\Delta T} = R_{th,eff}P$, and therefore $R_{th,eff} = d\overline{\Delta T}/dP$. The $\Delta T - P$ responses for the three suspended lengths are illustrated in Figure S4(a).

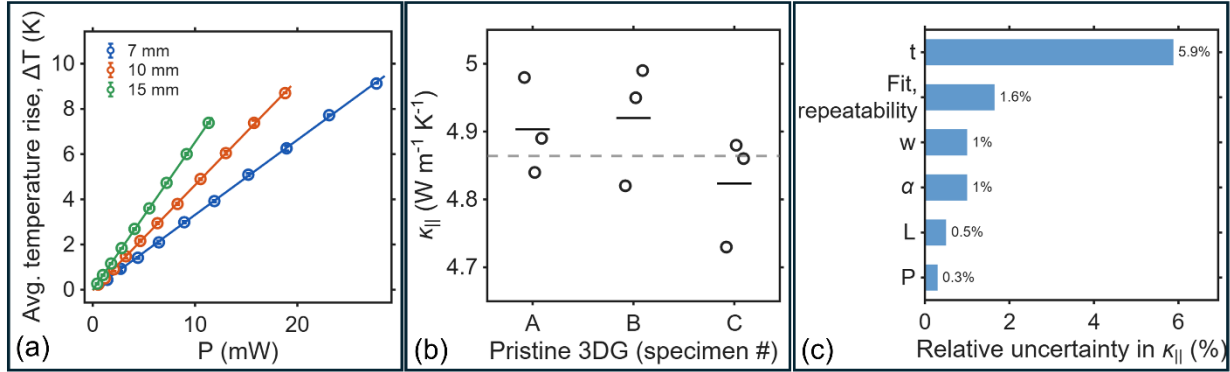


Figure S4. Suspended electrothermal in-plane thermal-conductivity measurement. (a) Resistance-derived average temperature rise as a function of electrical heating power for suspended 3DG specimen (b) Repeatability of $\kappa_{||}$ for pristine 3DG specimens (c) Relative contributions of the principal experimental and fitting parameters to the uncertainty in $\kappa_{||}$.

B. Heat-loss model and multi-length data reduction

For a uniformly Joule-heated suspended strip, axial conduction toward the two supports competes with distributed heat exchange with the surroundings. The steady-state one-dimensional temperature field was described by $\kappa_{||}A \frac{d^2\theta}{dx^2} - g\theta + \frac{P}{l} = 0$, where $\theta(x) = T(x) - T(0)$ and g is an effective distributed heat-loss conductance per unit length [$\text{W m}^{-1} \text{K}^{-1}$]. The coefficient g represents distributed environmental heat exchange, including convection and linearized radiation. The convection and radiation contributions were not independently fitted; instead, a combined effect was represented by the single effective parameter g . The supported ends were approximated as isothermal, consistent with the standard suspended-ribbon heat-balance model. Isothermal-end approximations are commonly employed in electrothermal measurements of suspended wire-like specimens.[10] Defining $m = \sqrt{\frac{g}{\kappa_{||}A}}$, the steady-state temperature distribution becomes

$\theta(x) = \frac{P}{gl} \left[1 - \frac{\cosh(mx)}{\cosh(ml/2)} \right]$. The corresponding average temperature rise is $\overline{\Delta T} = \frac{P}{gl} \left[1 - \frac{2}{ml} \tanh\left(\frac{ml}{2}\right) \right]$ and therefore $R_{th,eff} = \frac{1}{gl} \left[1 - \frac{2}{ml} \tanh\left(\frac{ml}{2}\right) \right]$. In the limit of negligible distributed loss, $g \rightarrow 0$, $\overline{\Delta T} = Pl/12\kappa_{||}A$, and $R_{th} = l/12\kappa_{||}A$. This limit helps inform why R_{th} is approximately proportional to l/A , while progressively larger deviations arise as environmental loss becomes important.

The three suspended lengths provide different sensitivities to g . For a trial value of g , can be inverted independently for each length to obtain $\kappa_{\parallel}(g)$. Because the strips correspond to the same material condition and were measured under nominally identical environmental conditions, a common pair $(\kappa_{\parallel}, g)$ is identified by simultaneous agreement among the three lengths. The representative pristine analysis in Figure 3(c) yields approximately $\kappa_{\parallel} = 4.864 \text{ W m}^{-1} \text{ K}^{-1}$ and $g = 0.0129 \text{ W m}^{-1} \text{ K}^{-1}$.

C. Boundary effects, reproducibility, and uncertainty

The four-probe configuration suppresses electrical contact resistance in the resistance thermometry but does not imply that thermal end-contact resistance is zero. In the present model, the supports are represented through the approximately isothermal end boundary condition. The use of multiple suspended lengths reduces sensitivity to localized end effects because of axial conduction and distributed environmental losses scale differently with specimen length. For multi-length fit, $\kappa_{\parallel} = f(l, w, t, \beta, P, R_{th,eff}, g)$,

and the combined uncertainty can be expressed as $u_c^2(\kappa_{\parallel}) = \sum_i \left(\frac{\partial \kappa_{\parallel}}{\partial x_i} u(x_i) \right)^2$. The

principal contributions are specimen length, width and thickness, resistance-temperature calibration, electrical power, the fitted $\overline{\Delta T} - P$ slope, and sensitivity of the common multi-length solution to g . Because $\kappa_{\parallel}$ and g are coupled fit parameters, uncertainty associated with the environmental-loss correction were evaluated from the multi-length solution.

References

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